PROPERTIES OF POLYMER-CARBON NANOTUBE COMPOSITES FABRICATED BY HIGH-SHEAR PROCESS

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1 Introduction
The weight reduction with enhanced mechanical properties has been a key in automotive industry during the last decades to deal with increasing environmental issue. From this perspective, carbon nanotube (CNT) in polymer matrix as a property-enhancer has a great potential comparing to conventional fillers because of their ability to act as a reinforcing phase at the nano-scale and their low density. However, dispersion of CNT in a polymer matrix has been limited due to strong inter-tube van der Waals’ force resulting in CNT aggregates in polymer matrix during mixing. These CNT aggregates impede enhancement of mechanical properties as well as other useful functions such as electrical conductivity.

It has been reported that shear stresses exerted on fillers during melt process determine the degree of dispersion of fillers [1-3]. This study demonstrates the effects of high shear on uniform dispersion of multiwalled carbon nanotube (MWNT) in thermoplastic polymer composites and enhancement of properties as a result of uniform dispersions.

2 Experiments
2.1 Materials and Sample Preparation
Polyamide 6 (PA6) pellets used in this work are commercially available with the grade name of 1027BRT, Hyosung Co., Korea. High purity MWNTs with different diameters were purchased from Showa Denko Co., Ltd., Japan. The average diameters of the tubes were each of 15 nm with average length of 3 um above 95% of purity and 150 nm with average length of 6 um above 99%.

PA6-MWNTs composites of different filler contents were prepared via a melt-compounding method using the high-shear extruder, NHSS2-28 (Niigata Machine Techno Co. Ltd., Japan). A feedback-type screw was adopted in this extruder. The L/D ratio of the screw was about 1.78. The melt compounding was carried out at 240℃ using the extruder with a single feedback-typed screw which is controllable for mixing time 120 sec and mixing speed to 3,000 rpm. The compounded samples were then extruded from a T-die.

2.2 Characterization
Fracture surfaces of the melt-compounded samples were observed by Field emission scanning electron microscopy (FE-SEM, JEOL JSM7500F) at an accelerating voltage of 10kV. The specimens were immersed in liquid nitrogen for 30 min and fractured. Two types of characterization apparatus were used in evaluating the electrical conductivity of the prepared composites depending on the conductivity of the samples. (For high resistivity: surface resistivity meter, 990SRM (Meech Co.Ltd., USA)). The ASTM standard dumb-bell-shaped specimens were prepared by injection molding apparatus. The stress-stain curves were measured using a tensile testing machine, Tensile UMT-300 (Orientec Co. Ltd., Japan), at a crosshead speed of 50 mm/min at 20 ℃ and 50% relative humidity.

3 Results and Discussion
3.1 Morphology Analysis
The morphologies of MWNTs with diameters of 15 nm (D15-MWNTs) and 150 nm (D150-MWNTs) used in this study are shown in Fig. 1. MWNTs of D15 are slightly curl-shaped due to their bigger aspect ratio compared to MWNTs of D150.
The smoothness of surface showed apparent difference as shown in Fig. 2 and this can be a good indicator to estimate the degree of dispersion of fillers. It is clear that the MWNTs of the composite by high speed are well and miscible-like dispersed in polymer compared with the one by low speed.

To investigate the effect of melt-mixing time, the PA6 composites with D15-MWNTs at 3 wt% loading were prepared by different mixing speeds for 120 sec. As melt-mixing time goes longer, the surface of all specimens became very smoother compared with one by shorter mixing time of 20 sec.

Electrical conductivity can be increased when uniformly dispersed fillers in polymer matrix contact each other forming a percolation network. Therefore, measuring surface resistivity is another mean to evaluate the degree of dispersion of fillers. Fig. 3 shows the relationship among the surface electrical resistance, the loading content, and the melt-mixing speed on the PA6 composites with D15-MWNTs. As shown in the pictures, as the mixing speed increases, the electrical percolation became earlier. Moreover, no any drop on surface resistivity for all the specimens by 300 rpm happens in spite of increasing the loading content.

The electrical conductivity of the PA6 composites with D15-MWNTs of 3 wt% loading by different mixing speeds and times was investigated. As a result, the surface resistivity depends on the mixing speed and mixing time. Independent of mixing time, the specimens by the mixing speed of 300 rpm have no change on the surface resistivity.

To investigate the effect of melt-mixing time on the electrical conductivity, the PA6 composites with D15-MWNTs at 3 wt% loading were prepared by different mixing speeds for 20 sec and 120 sec, respectively. As shown in Fig. 4, surface resistivity decreased from $10^9 \Omega$/sq to $10^6 \Omega$/sq at 1500 rpm as mixing time increased to 120 sec. This shows that improved dispersion of CNT at longer mixing time was obtained at relatively lower mixing speed. No significant difference on surface resistivity was found between mixing time 20 and 120 sec. As a result, two facts that critical amount of shear force on CNT exists for the uniform dispersion and that the amount can be given by mixing conditions were confirmed.

A percolation threshold of CNT is the critical concentration forming a three dimensional network of CNT in polymer matrix. In general, when the concentration of CNT approaches percolation threshold (1 ~ 3 wt%), physical properties such as...
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electrical and thermal conductivities as well as mechanical properties are improved. Therefore, mechanical properties can be used to expect the percolation threshold of CNT for the effective network for electrons to be transferred through entangled CNTs in polymer matrix.

Fig. 4 Surface electrical resistances of PA6 composites with D15-MWNTs of 3 wt% loading by different mixing speeds and times

Table 1 presents the Young’s modulus and stress at break of composites with different processing conditions. From the results, it is clearly demonstrated that D150-MWNTs increase the mechanical properties of the composites compared with D15-MWNTs. This result is attributed to the stiffness and easy dispersed property due to low aspect ratio and much bigger diameter of tubes.

Table 1 Young’s Modulus and stress at break of Composites with different processing conditions [(a)D15-MWNTs, (b)D150-MWNTs]

<table>
<thead>
<tr>
<th>System Processing</th>
<th>Young’s Modulus (GPa)</th>
<th>Stress at break (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PA6/(a)-0.5%-3000r-20s</td>
<td>1.564</td>
<td>49.85</td>
</tr>
<tr>
<td>PA6/(a)-3.0%-3000r-20s</td>
<td>1.757</td>
<td>53.85</td>
</tr>
<tr>
<td>PA6/(b)-0.5%-3000r-20s</td>
<td>2.110</td>
<td>63.07</td>
</tr>
<tr>
<td>PA6/(b)-3.0%-3000r-20s</td>
<td>1.792</td>
<td>57.29</td>
</tr>
</tbody>
</table>

Flexural strength and modulus of neat PA6 and composites with different processing conditions were also investigated. As shown in table 2, the higher shear rate applied, the better dispersion of CNT obtained resulting in higher flexural strength and modulus. At the same shear rate, the concentration of CNT has no significant effect on flexural strength and modulus. Unprecedentedly, a flexural strength of a composite containing only 0.1 wt% loading of MWNTs shows a dramatic increase. Even though further analytic studies about this phenomenon are required, it can be inferred hypothetically that significant increased strength was caused by extremely high shear rate above 1000 sec⁻¹ and effectively dispersed CNT acting as a nucleating agent. And small-sized crystalline domains stimulated by dispersed CNT particles may lead to significant increase in flexural strength. The effects of high shear rate on these properties will be studied in the near future.

The effective dispersion of CNT within a restricted volumetric space was impeded when the concentration of CNT was higher than 3 wt% resulting in relatively lower increases ratio. While entangled or aggregated CNT bundles show good electrical conductivity, these bundles sometimes exhibit negative effects from the perspective of mechanical property. An effective transferring electrons through the entangled CNT network promises lower surface resistivity as shown in Fig 4. But this does not mean that uniform dispersion for good mechanical properties was obtained.

Table 2 Flexural strength and modulus of neat PA6 and composites with different processing composite

<table>
<thead>
<tr>
<th>wt %</th>
<th>High shear zone (°C)</th>
<th>Flexural Strength</th>
<th>Flexural Modulus</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Temp (°C)</td>
<td>Shear rate (s⁻¹)</td>
<td>Time (s)</td>
</tr>
<tr>
<td>1</td>
<td></td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>2</td>
<td>3</td>
<td>260</td>
<td>1760</td>
</tr>
<tr>
<td>3</td>
<td>5</td>
<td>260</td>
<td>1760</td>
</tr>
<tr>
<td>4</td>
<td>0.1</td>
<td>260</td>
<td>1760</td>
</tr>
<tr>
<td>5</td>
<td>0.1</td>
<td>260</td>
<td>1760</td>
</tr>
<tr>
<td>6</td>
<td>0.1</td>
<td>290</td>
<td>2930</td>
</tr>
</tbody>
</table>

* The same conditions for all samples were used for a melting zone (@ 260°C and 150 rpm)
4 Conclusions

Well-dispersed CNT embedded PA composites were prepared using a high shear extruder and the degree of dispersion of CNT were investigated by examining physical properties such as electrical conductivity and mechanical properties. As a result, it can be concluded that high shear is one of the key issues in melt processing to approach the uniform dispersion and good physical properties can be achieved by controlling processing parameters in melt processes.

References